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# RESEARCH MEMORANDUM

THE USE OF METALLIC INHIBITORS FOR ELIMINATING  
MASS TRANSFER AND CORROSION IN NICKEL  
AND NICKEL ALLOYS BY MOLTEN  
SODIUM HYDROXIDE

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RESEARCH MEMORANDUMTHE USE OF METALLIC INHIBITORS FOR ELIMINATING MASS TRANSFER  
AND CORROSION IN NICKEL AND NICKEL ALLOYS

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## SUMMARY

The effectiveness of chromium and aluminum as inhibitors for mass transfer and corrosion in nickel and nickel alloys by sodium hydroxide was studied under free convection and at fluid velocities of 15 feet per second. Although no previous additive has reduced mass transfer significantly, the addition of 1 percent by weight of 325-mesh chromium powder to the caustic essentially eliminated the transfer for 50 hours at 1500° F with a temperature difference of 20° F and a flow of 15 feet per second. An experimental run for 250 hours with a 40° F temperature difference indicated that a 1 percent addition of chromium would not protect the system indefinitely. Chromium additions of 1 to 5 percent resulted in essentially complete elimination of mass transfer from a specimen in nickel under free-convection conditions for 96 hours at 1500° F with a temperature difference of 45° F. Similar results were obtained with monel under free-convection conditions. These results indicate the desirability of further tests with monel under forced circulation. The protective action of the additive is hypothesized to be due to its reaction with the caustic, forming hydrogen in all portions of the system in quantities large enough to inhibit the reaction between the hydroxide and nickel.

## INTRODUCTION

The extreme desirability of sodium hydroxide as a moderator-coolant for high-temperature reactor application has led to an extensive search for a suitable container material. Sodium hydroxide is very corrosive in the temperature range of interest, and at 1500° F causes extensive

intergranular penetration and mass transfer if a temperature gradient is present. The best container material found to date is nickel; in this metal the caustic produces mass transfer without intergranular attack.

A hydrogen atmosphere has been found (refs. 1 and 2) to reduce the extent of transfer to a marked degree in static systems. However, little benefit has been gained by the use of a hydrogen atmosphere in circulating loop experiments. Preliminary experiments at the Lewis laboratory, described in reference 3, indicated that mass transfer could be considerably reduced in static crucibles by the addition of small quantities of finely powdered chromium or aluminum metal to the caustic.

This report presents the results of an extension of the investigation concerning the effectiveness of chromium and aluminum for reducing mass transfer in nickel and nickel alloys. Static crucible studies were carried out at 1500° F with a hot-to-cold temperature difference  $\Delta T$  of 45° F. The alloys studied were Inconel, monel, AISI 347 SS, Nimonic 80A, and Nimonic 90. The use of chromium in various forms was investigated. The effects of chromium and aluminum on mass transfer in an induced circulation system, the NACA Toroid Circulating Apparatus, were studied at 1500° F with temperature differences of 20° and 40° F. These tests were carried out in nickel toroids. A hypothesis for the mechanism by which the mass transfer is reduced is described.

#### EXPERIMENTAL PROCEDURES

Static crucibles. - The static crucible experiments were carried out according to the procedures described in reference 3. A diagram of the static crucible is shown in figure 1. The crucibles were mounted in a furnace that provided a hot-zone temperature of 1500° F at the bottom of the crucible and a temperature drop of 45° F from the bottom to the liquid level. Aluminum and chromium were introduced as 325-mesh powder into separate crucibles after the occluded water and air were removed by heating and evacuation. Chromium was also introduced as an electroplated surface on the interior of some crucibles. Several plated crucibles were tested after the chromium had been diffused into the nickel by a vacuum heat treatment for 3 hours at 2300° F. The possible effects of trace elements in monel were investigated by testing nickel crucibles into which a copper electroplate had been diffused by vacuum heat treatment at 1600° F for 3 hours.

The weight changes of disk specimens in the hot zone were used as a measure of the extent of intergranular attack and/or mass transfer. These data together with metallographic studies of sections through the specimens were used to determine the effectiveness of the various treatments.

Toroid test. - The toroid circulating apparatus and experimental procedure are described in references 4 and 5. A diagram of the apparatus is shown in figure 2. Aluminum and chromium were added in the form of 325-mesh powder to separate nickel toroids before the water and air were removed by evacuation. Tests were run at 1500° F with temperature differences of 20° and 40° F using additions of 1 percent chromium. A temperature difference of 20° F was used in the experiment using 1 percent aluminum addition and in the experiment with no additive. The flow velocity was 15 feet per second in all the experiments.

The course of mass transfer was detected at intervals during the experiment by means of X-ray shadowgraphs of the cooled section. In order to obtain these, the circulation and heating were stopped and the toroid on its mounting plate was suspended so that the caustic drained out of the cooled section. After the caustic had frozen, the X-ray shadowgraph was taken. The toroid was then returned to the circulating apparatus and the test resumed. The average inside diameter was determined from a series of 21 measurements on each shadowgraph. The reciprocal of this average diameter was taken as a measure of the course of mass transfer during the experiment.

When the test was finally terminated, the caustic was removed by dissolving in water and sections of equal length were removed from the hot and cold sections. The ratio of the cold-to-hot section weights was used as a final measure of the extent of mass transfer.

## RESULTS

Static test. - The results obtained in static capsules are presented in table I. The initial data reported in reference 3 for chromium and aluminum additions are included for purposes of comparison. Experiments of 96 hours duration with aluminum additions confirmed the initial results. Concentrations of 1 and 1.5 percent could be run without leakage, while higher concentrations led presumably to hydrogen pressures that caused the capsules to burst. The fact that the weight loss was greater for 1 percent addition at 96 hours than at 24 hours, coupled with the lower weight loss for 1.5 percent addition at 96 hours, leads to the conclusion that the aluminum was effective until it was used up. An attempt to reduce the reactivity of the aluminum by incorporation with nickel to form the 6 weight-percent alloy NiAl did not improve its performance. Crucibles and specimens of NiAl exhibited extensive intergranular attack in addition to mass transfer.

The results of 96-hour tests with chromium were as good as the 24-hour results obtained earlier. Metallographic examination indicated that no intergranular attack had occurred. The specimens appeared to be coated, and the weight gains indicated that the coating was negligible (of the order of 0.1 to 0.4 mil in thickness).

Incorporation of chromium as an electroplate yielded satisfactory results. No mass-transfer deposit was obtained, and the specimen weight losses can be attributed solely to the reaction of the chromium plate with the caustic.

The experiments with crucibles in which the chromium plate had been diffused into the nickel were unsuccessful, since all the crucibles failed by bursting by generated gas pressure. No mass transfer was visible, but intergranular attack occurred.

Efforts to improve alloy behavior by the use of the Nimonic alloys that contain higher percentages of chromium and less iron than do Inconel or the stainless steels also led to failure. In all cases extensive intergranular attack occurred, although very little mass transfer was noted.

Attempts to limit intergranular attack by addition of sacrificial chromium to AISI 347 stainless steel and Inconel were not successful.

The experiments with monel indicate that it behaves in much the same fashion as nickel. Specimen weight loss for 24 hours was of the same order of magnitude as that for nickel (9.0 mg as compared with 5.0 mg for Ni) with no intergranular attack. A 3 percent addition of powdered chromium yielded results equally as good as those for nickel crucibles. Copper-plated nickel and nickel with copper diffused into it both yielded results equivalent to those for monel.

Toroid test. - The results of induced flow experiments in nickel toroids are presented in table II and figure 3. Previous results with various additives are included for comparison. Chromium addition proved effective, while aluminum did not. The data using 1 percent chromium additions for 24 and 50 hours with a  $\Delta T$  of  $20^{\circ}$  F indicate that mass transfer was essentially eliminated.

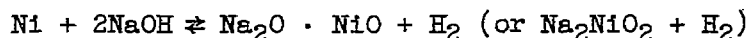
The experiment with a  $40^{\circ}$  F  $\Delta T$  was partly interpreted on the basis of X-ray examination. The shadowgraphs in figure 4 show no visible accumulation of deposit for a period of 150 hours. When the experiment was terminated after 250 hours, the cold section was found to contain a mass-transfer deposit that was very small in quantity. However, there was another type of deposit distributed throughout the entire system. It consisted of metal granules, which analysis showed to contain 98.4 percent nickel and 0.03 percent chromium. These granules were approximately spherical and showed only slight adherence to the walls. This granular material may have been carried along by the molten caustic. The presence of this granular material in the hot section made it impossible to obtain a meaningful cold-to-hot section weight ratio. However, the use of the average internal diameter of the cold section obtained from the shadowgraphs permitted the course of mass

transfer to the cold section to be compared with the behavior when no additive was used. In figure 5, the reciprocal of the average inside diameter of the cold section is plotted as a function of running time.

It is to be noted that the 250-hour test was run with a temperature difference of 40° F. Previous work under free-convection conditions reported in reference 6 showed the mass-transfer rate to be almost linearly dependent on the hot-to-cold section temperature difference for small values of  $\Delta T$ . It might be expected that a similar dependence exists under flow conditions. On this basis, the result for 250 hours at a 40° F  $\Delta T$  may be approximately equivalent to that for 500-hour operation at a  $\Delta T$  of 20° F.

#### DISCUSSION

The reaction mechanism proposed in references 7 and 8 is a reasonable explanation of the mode by which nickel reacts with sodium hydroxide. In the reaction between the caustic and metal, hydrogen and a mixed oxide or nickelite is formed:

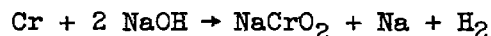


In the cold zone, the equilibrium is shifted to the left; the mixed oxide behaves as if it were the two separate compounds NiO and Na<sub>2</sub>O, since the NiO is reduced at a more rapid rate than the Na<sub>2</sub>O. The loss of hydrogen through the nickel vessel walls and the difference in the rates of reduction for the two oxides lead to an apparently selective reduction of NiO to Ni in the cold zone; therefore, mass transfer results.

The law of mass action dictates that an increase of hydrogen pressure will decrease the reaction between the caustic and nickel. Experiments reported in references 1 and 2 indicated that mass transfer could be reduced by a large factor if a hydrogen atmosphere were maintained above the caustic. Complete elimination of mass transfer was not attained. Experiments in thermal convection loops (ref. 9) indicated that hydrogen was ineffective when long distances separated the hydrogen atmosphere from the caustic-metal interfaces.

These facts and the data obtained in this investigation are in agreement with the hypothesis that chromium and aluminum are effective because they react with sodium hydroxide to form hydrogen. The 325-mesh powder is fine enough to be carried along by convection, and thus both the powder and the chromium plate generate hydrogen throughout the whole system. Effective suppression of the nickel-caustic reaction results at

all metal-caustic interfaces. The fact that sodium was found to be a reaction product is also consistent with these reactions:



The rate of reaction with aluminum is so great that the pressure builds up to a high value, despite the permeability of nickel to hydrogen. The success of the chromium may be assumed due to a balance between the reaction rate and the rate of hydrogen loss through the walls. The resultant hydrogen pressure is high enough to be effective but not high enough to burst the tubing.

This mechanism also provides an explanation for the results observed with nickel alloys containing chromium. In this case, the reaction of caustic with the chromium results in the inhibition of the reaction with nickel and thus reduces or eliminates mass transfer. However, the reaction with chromium results in intergranular attack.

#### SUMMARY AND CONCLUSIONS

Static crucible experiments with sodium hydroxide at 1500° F and a temperature difference of 45° F were conducted in nickel, monel, Inconel, AISI 347 stainless steel, Nimonic 80A, and Nimonic 90. The effects on mass transfer and corrosion by additions of small quantities of chromium and aluminum were studied. Studies in nickel toroids at a fluid velocity of 15 feet per second were conducted in the NACA Toroid Circulating Apparatus at 1500° F with a temperature difference of 20° and 40° F. The results of the investigation may be summarized as follows:

1. Mass transfer and corrosion were essentially eliminated for 50 hours in the nickel toroid operated with a temperature difference of 20° F and a 1 percent addition of 325-mesh chromium powder.

2. A 250-hour toroid test with a 40° F temperature difference resulted in a small mass-transfer deposit. The additional formation of metal granules indicated that 1 percent addition of chromium would not protect a nickel system indefinitely. It also indicated that when the chromium is used up, further metal deposition may be in the form of relatively nonadherent granules.

3. Mass transfer and corrosion from specimens were eliminated with chromium inhibitor in 96-hour static tests at 1500° F with a temperature difference of 45° F.

4. Static crucible tests indicate that monel with a chromium inhibitor is essentially as good as pure nickel plus the inhibitor for containing sodium hydroxide at 1500° F.

5. Static tests with chromium present as an electroplate showed that this method of introducing the inhibitor may also be effective.

6. Aluminum additions are also effective for short times, but the rapid reaction rate causes the generation of excessive hydrogen pressures.

7. The mechanism of this type of inhibition is hypothesized to be due to the generation of hydrogen in all parts of the system in quantities large enough to inhibit the reaction between the sodium hydroxide and nickel.

The proposed mechanism would lead to the prediction that possible adjustments in the caustic-inhibitor reaction rate might be necessary to compensate for variations in hydrogen diffusion rate from one system to another. These adjustments might be accomplished by the use of metal inhibitors that would react with the caustic at different rates. Possible choices are vanadium, titanium, and manganese.

Lewis Flight Propulsion Laboratory  
National Advisory Committee for Aeronautics  
Cleveland, Ohio, December 7, 1954

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TABLE I. - RESULTS OF STATIC CRUCIBLE TESTS AT 1500° F WITH A  $\Delta T$  OF 45° F

| Crucible material | Additive                           | Test duration, hr | Specimen weight change, mg | Other observations  |
|-------------------|------------------------------------|-------------------|----------------------------|---|
| Nickel            | None                               | 24                | -5.0                       | Mass transfer, no intergranular attack                                      |
|                   | None                               | 96                | -28.0                      |   |
| Nickel            | Al, 1 percent                      | 24                | -1.0                       | Concentrations higher than 1.5 percent resulted in tube failure by bursting |
|                   | Al, 1 percent                      | 96                | -18.1                      |   |
|                   | Al, 1.5 percent                    | 96                | -3.5                       |   |
| NiAl              | None                               | 24                | -9.7                       | Extensive intergranular attack  |
| Nickel            | Cr, 1 percent                      | 24                | 2.4                        | No intergranular attack, very thin coating on specimens                     |
|                   | Cr, 3 percent                      | 24                | 2.9                        |   |
|                   | Cr, 5 percent                      | 24                | 1.3                        |   |
|                   | Cr, 1 percent                      | 96                | .9                         |   |
|                   | Cr, 3 percent                      | 96                | 5.4                        |   |
|                   | Cr, 5 percent                      | 96                | 10.1                       |   |
| Nickel            | Cr, plate                          | 24                | -99.5                      | No visible mass transfer  |
| Nickel            | Cr, diffused                       | 24                | (a)                        | Intergranular attack  |
| Nimonic 80A       | None                               | 24                | 53.9                       | Extensive intergranular attack, no mass transfer                            |
| Nimonic 90        | None                               | 24                | 55.3                       | Extensive intergranular attack, no mass transfer                            |
| 347 SS            | None                               | 24                | 33.0                       | Extensive intergranular attack, no mass transfer                            |
| 347 SS            | Cr, 3 percent                      | 24                | 57.5                       | Extensive intergranular attack, no mass transfer                            |
| Inconel           | None                               | 24                | 56.2                       | Extensive intergranular attack, no mass transfer                            |
| Inconel           | Cr, 3 percent                      | (a)               |                            |   |
| Inconel           | Cr, plate                          | 24                | 7.2                        | Extensive intergranular attack, no mass transfer                            |
|                   | Weight of Cr plate on specimen, mg | 24                | 16.5                       |   |
|                   |                                    | 24                | 21.6                       |   |
|                   |                                    | 24                | 39.5                       |   |
| Monel             | None                               | 24                | -9.0                       | Mass transfer, no intergranular attack                                      |
| Monel             | Cr, 3 percent                      | 24                | 1.9                        | Mass transfer, no intergranular attack                                      |
| Nickel            | Cu, plate                          | 24                | -8.5                       | Mass transfer, no intergranular attack                                      |
| Nickel            | Cu, diffused                       | 24                | -6.7                       | Mass transfer, no intergranular attack                                      |

\*Burst.

TABLE II. - RESULTS OF TOROID TEST IN NICKEL AT 1500° F

WITH FLUID VELOCITY OF 15 FEET PER SECOND

| Additive                   | Test duration, hr | Cold-to-hot section weight ratio |
|----------------------------|-------------------|----------------------------------|
| None                       | 24                | 1.090                            |
| None                       | 91                | 1.5659                           |
| Al, 1 percent              | 24                | 1.4313                           |
| Cr, 1 percent              | 24                | 1.0042                           |
| Cr, 1 percent              | 50                | 1.0056                           |
| Cr, 1 percent              | 53.4              | 1.0008                           |
| Cr, 1 percent <sup>a</sup> | 250               | -----                            |

<sup>a</sup> $\Delta T = 40^{\circ}$  F.

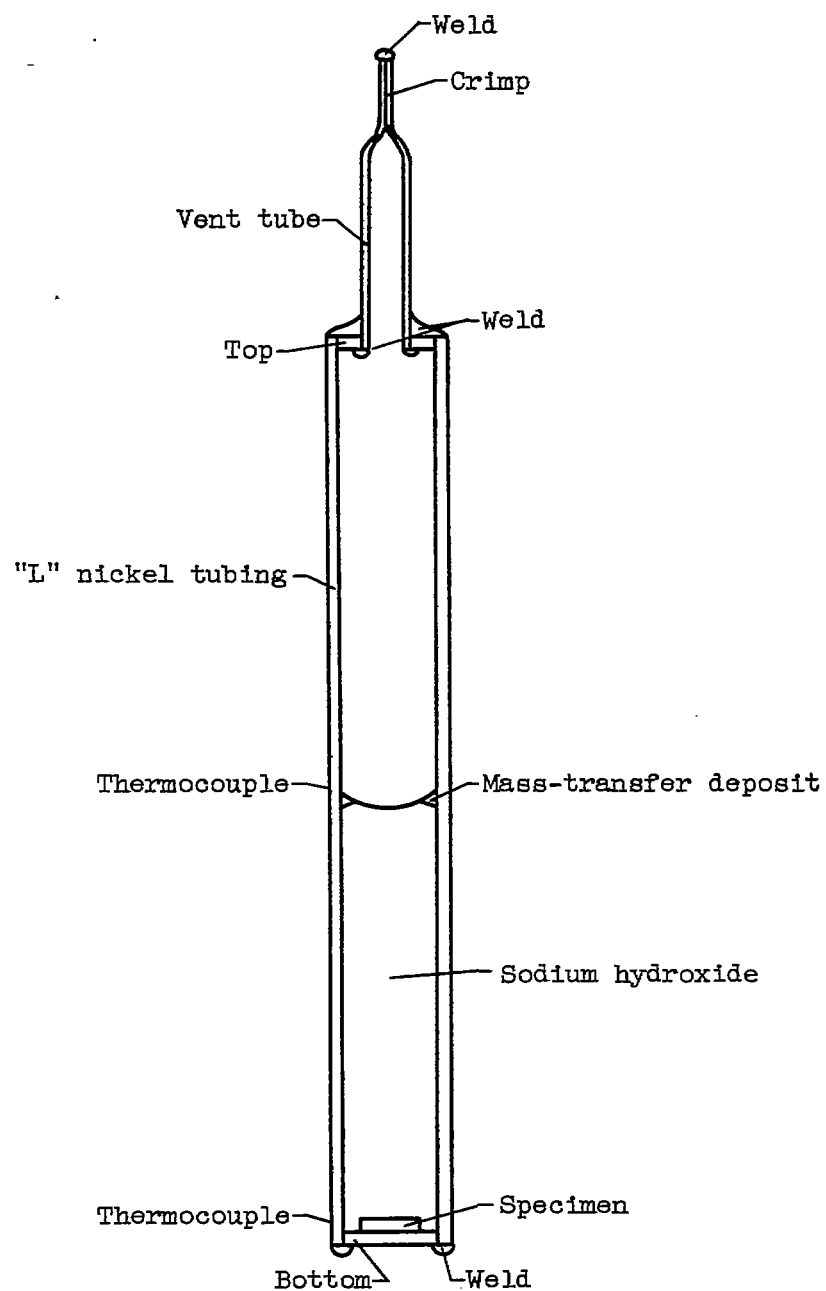


Figure 1. - Static crucible.

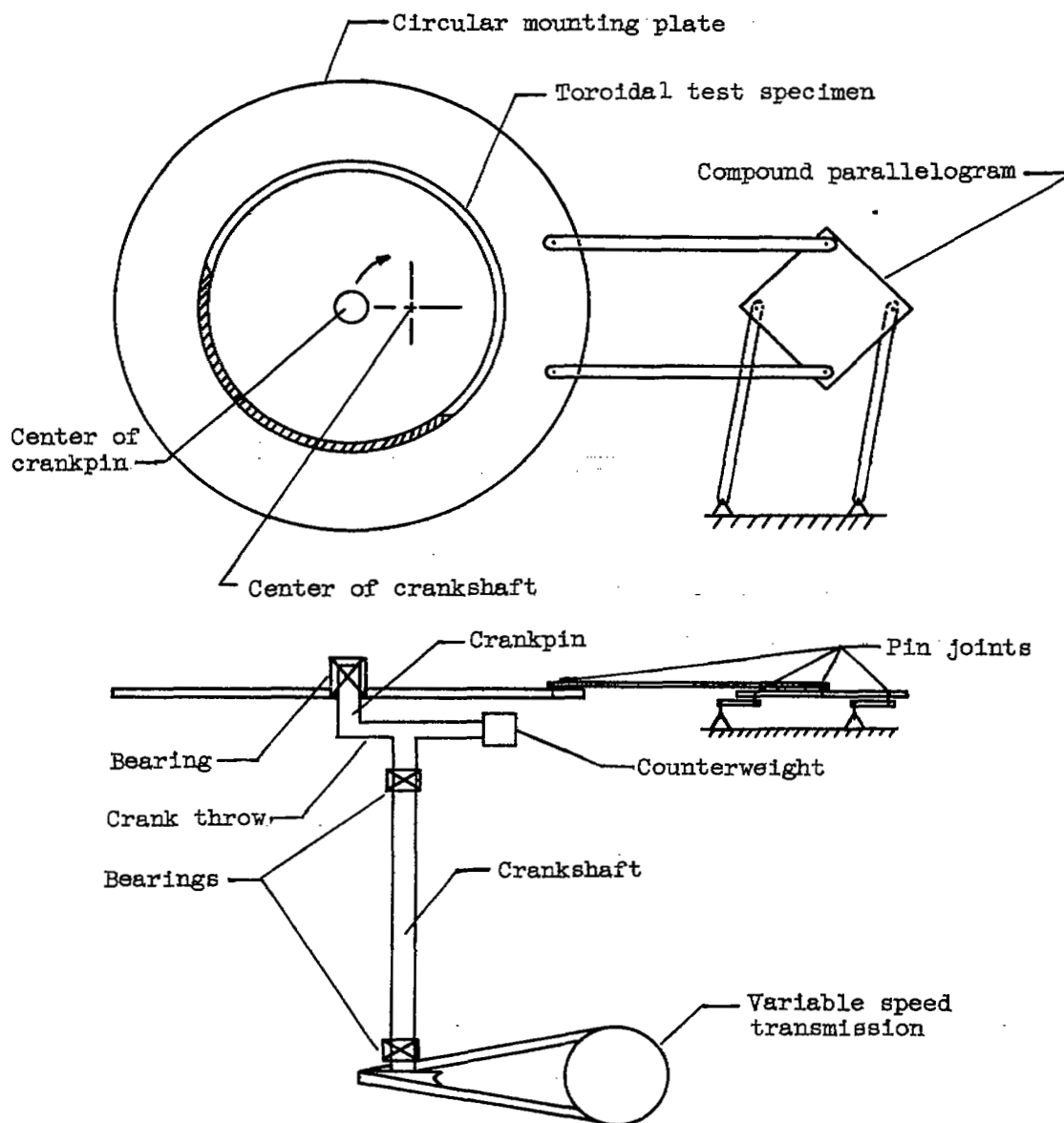


Figure 2. - Schematic diagram of circulating apparatus.

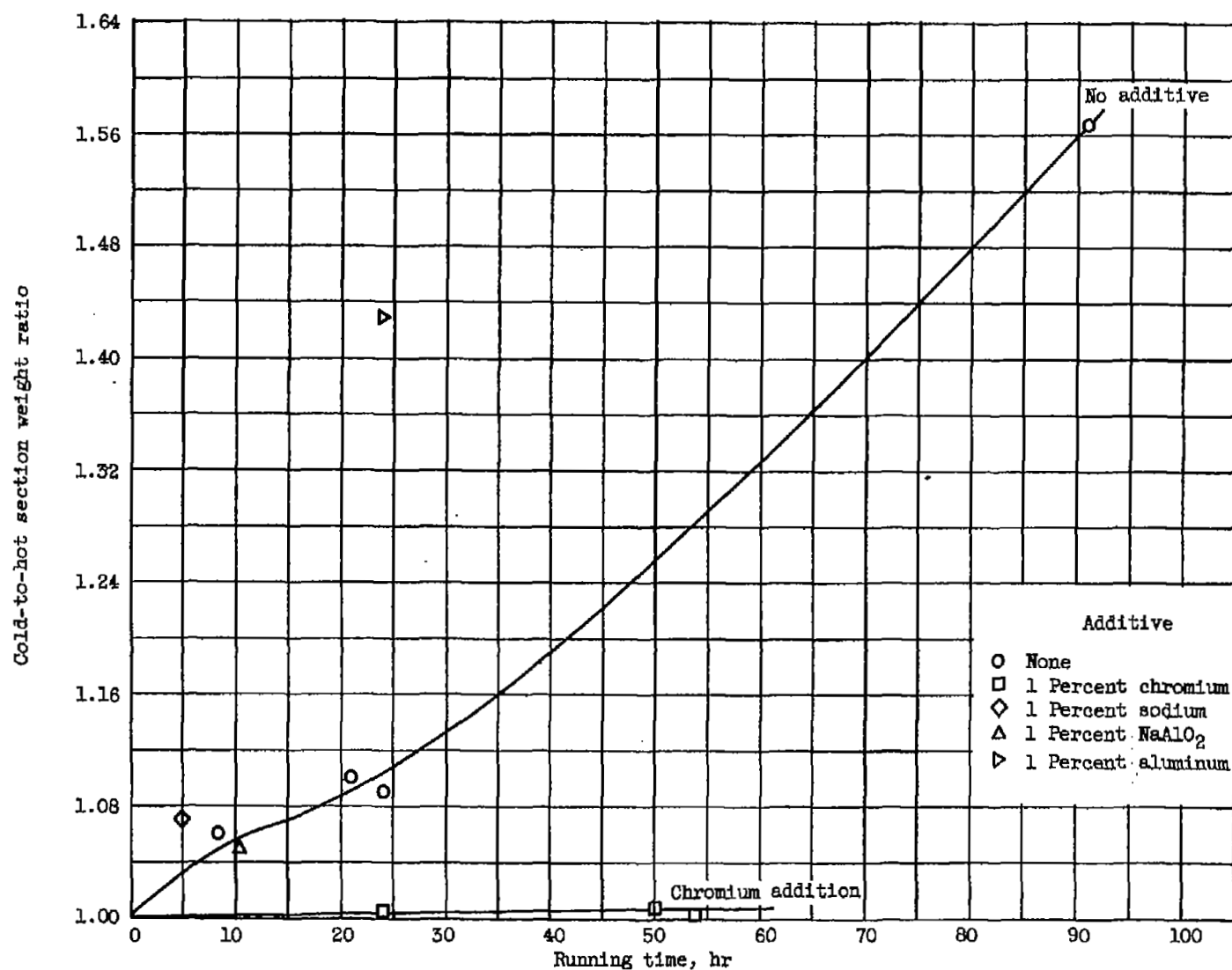
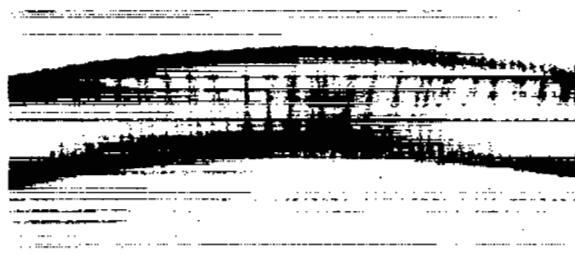


Figure 3. - Cold-to-hot section weight ratios obtained on termination of toroid experiments run in nickel at 1500° F with  $\Delta T$  of 20° F and fluid velocity of 15 feet per second.



Before operation

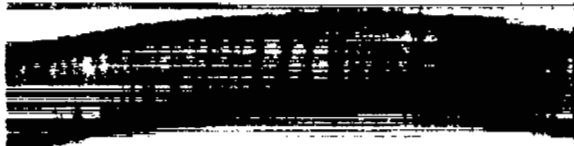


After 150 hours operation



After 250 hours operation

(a) 1% addition of chromium powder, run at 1500°F and 15 feet per second with  $\Delta T$  of 40°F.



After 48 hours operation



After 91 hours operation

(b) No additive, run at 1500 F and 15°feet per second with  $\Delta T$  of 20°F.

Figure 4. - X-ray shadowgraphs of cold sections of toroids run with and without chromium addition.

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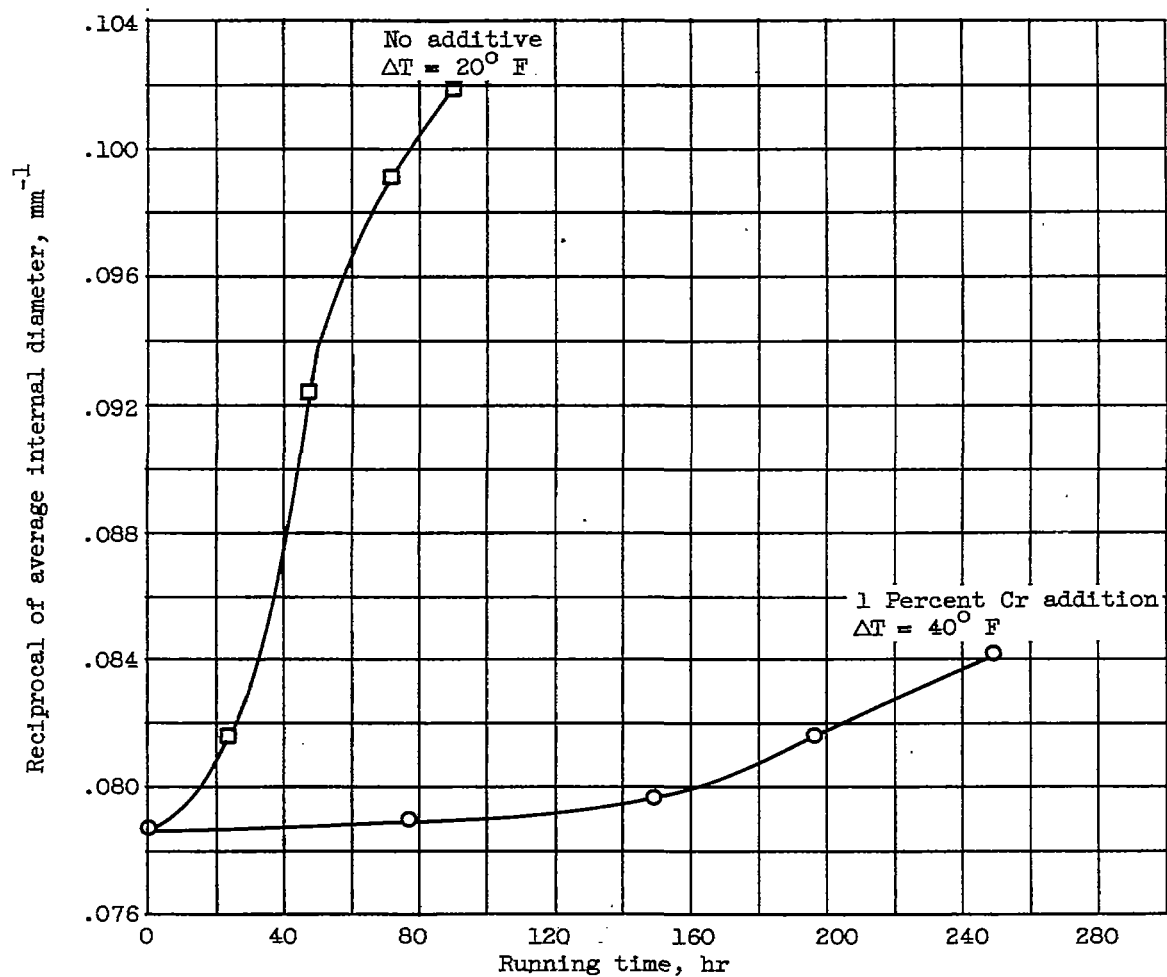


Figure 5. - Reciprocal of average internal diameter of cold section against running time for nickel toroids operated at 1500° F and fluid velocity of 15 feet per second.





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